Polymerization of olefins

The present invention relates to a process for the polymerization
of olefins and to a catalyst system suitable for this purpose.

Catalyst systems having a uniquely defined, active center, known
as single-site catalysts, are gaining increasing importance in
the polymerization of olefins. These catalyst systems lead to
polymers having narrow molecular weight distributions, which
results in particularly favorable mechanical properties. Among
these single-site catalysts, the metallocene catalysts have
hitherto achieved particular industrial importance. Appropriate
substitution on the cyclopentadienyl ligands of these can
influence the polymer properties. However, many metallocene
catalysts can be obtained only by multistage syntheses and
therefore represent a considerable cost factor in olefin
polymerization.

Substituted and unsubstituted triazacycloalkanes having different
ring sizes have been known for a long time. Many of them can be
prepared simply and inexpensively. These ligands also coordinate
well to metal ions to form stable complexes of which some possess
unusual chemical and physical properties. Of particular interest
here is the high stability of these coordinated ligands - an
important aspect in the selection of suitable ligand systems for
potential polymerization-active complexes (G. J. P. Britovsek, V.
C. Gibson, D. F. Wass, Angew. Chem. 1999, 111, 448-468). Thus, it
is known that N,N',N''-trialkyl-1,4,7-triazacyclononanerhodium
compounds (Wang and Flood, Organomet. 15, (1996), 491-498) and
-chromium compounds (G. P. Stahley et al., Acta Crystall. C51,
(1995), 18-20) will polymerize or oligomerize ethene. However,
the polymerization rate is very low.

Introduction of donor-functionalized side chains which bind
intramolecularly to the transition metal into these
triazacycloalkane ligands enables the properties of the
corresponding metal complexes to be significantly altered. Thus,
a change in the redox potential or the coordination behavior of
further ligands has been observed as a result (T. Kaden, Topics
Curr. Chem. 121, (1984), 157-179). Complexes of this type have
hitherto not been used for the polymerization of olefins.

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It is an object of the present invention to find a process for the polymerization of olefins which is based on a catalyst system which has good polymerization activity and is simple to prepare and to modify.

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We have found that this object is achieved by a process for the polymerization of olefins, which comprises carrying out the polymerization in the presence of catalysts comprising the following components:

10
(A)   at least one complex of a transition metal with a tridentate macrocyclic ligand which bears at least one substituent having a donor function and

15 (B)   if desired, one or more activator compounds.

Furthermore, we have found a catalyst system comprising the following components:

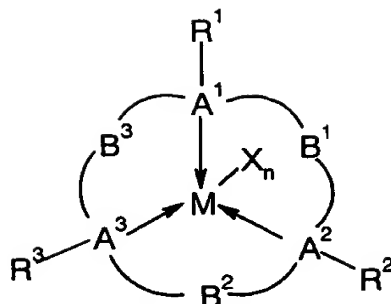20 a)   at least one transition metal complex (A) as set forth above and

b)   at least one activator compound (B).

25 The tridentate macrocyclic ligand can be bound to the transition metal via nitrogen, phosphorus, oxygen or sulfur. The donor function can be uncharged or anionic and contain a heteroatom of groups 15-16 of the Periodic Table (as defined in IUPAC proposal of 1985) or be a carbanion. The donor is joined to the
30 macrocyclic ligand via a bridge, so that from 1 to 8, preferably from 1 to 3, bridge members which comprise carbon or silicon and may be substituted form the direct linkage, but not more than two silicon atoms are in each case adjacent to one another. The functional substituent can be uncharged or anionic. If it is
35 uncharged, it can be bound coordinatively to the transition metal center M or may not coordinate. It is preferably coordinated to the metal center M. If the functional substituent is formally anionic, it is covalently bound to the metal center. The bonds can be intramolecular or intermolecular, preferably
40 intramolecular. During the polymerization, it may also be possible for one or more of the functional substituents to bind coordinatively or covalently to the activator compound.

In one embodiment of the process of the invention, the transition
45 metal complex (A) used is a compound of the formula I

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$$
\begin{array}{c}
R^1 \\
| \\
A^1 \\
B^3 \quad \quad B^1 \\
\quad \quad X_n \\
A^3 \longrightarrow M \longleftarrow A^2 \\
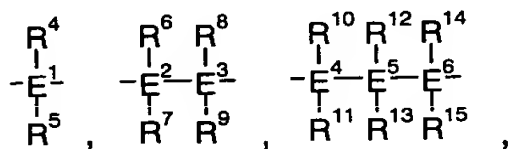R^3 \quad \quad \quad R^2 \\
B^2
\end{array}
$$

I

where the variables have the following meanings:

M   is a transition metal of groups 3 to 12 of the Periodic
         Table,

B^1–B^3 are each a divalent radical selected from the group
         consisting of

$$
-\overset{\overset{\displaystyle R^4}{|}}{\underset{\underset{\displaystyle R^5}{|}}{E^1}}- \qquad
-\overset{\overset{\displaystyle R^6}{|}}{\underset{\underset{\displaystyle R^7}{|}}{E^2}}-\overset{\overset{\displaystyle R^8}{|}}{\underset{\underset{\displaystyle R^9}{|}}{E^3}}- \qquad
-\overset{\overset{\displaystyle R^{10}}{|}}{\underset{\underset{\displaystyle R^{11}}{|}}{E^4}}-\overset{\overset{\displaystyle R^{12}}{|}}{\underset{\underset{\displaystyle R^{13}}{|}}{E^5}}-\overset{\overset{\displaystyle R^{14}}{|}}{\underset{\underset{\displaystyle R^{15}}{|}}{E^6}}- \quad ,
$$

where

E^1–E^6 are silicon or carbon and not more than two of E^4–E^6 are
         silicon,

A^1–A^3 are nitrogen or phosphorus,

R^1–R^{15} are hydrogen, C_1–C_{20}-alkyl, 5- to 7-membered cycloalkyl
         which may in turn bear a C_6–C_{10}-aryl group as
         substituent, C_2–C_{20}-alkenyl, C_6–C_{20}-aryl, alkylaryl having
         from 1 to 10 carbon atoms in the alkyl part and 6-20
         carbon atoms in the aryl part, $SiR^{32}{}_3$ or a radical of the
         formula $-Z-D$, where the organic radicals R^1–R^{15} may be
         substituted by halogen(s) and any two geminal or vicinal
         radicals R^1–R^{15} may also be joined to form a five- or
         six-membered ring, and at least one of the radicals
         R^1–R^{15} is a radical $-Z-D$, where D is a functional group
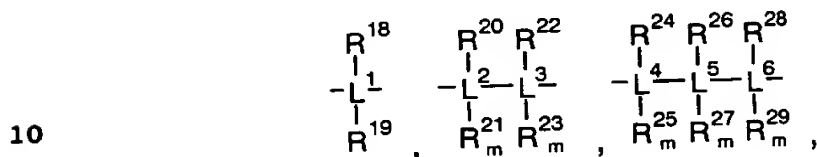   having the following meanings:

D   is $NR^{16}R^{17}$, NR^{16}, OR^{16}, O, SR^{16}, S, $PR^{16}R^{17}$, SO_3R^{16},
         $OC(O)R^{16}$, CO_2, $C(O)R^{16}$, $C(NR^{16})R^{17}$, CN or a five- or
         six-membered heterocyclic ring system, where the radicals

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$R^{16}-R^{17}$ may also be joined to Z to form a five- or six-membered ring;

Z   is a divalent radical selected from the group consisting of:

$$-\overset{\displaystyle R^{18}}{\underset{\displaystyle R^{19}}{L^1}}- \qquad -\overset{\displaystyle R^{20}}{\underset{\displaystyle R^{21}_m}{L^2}}-\overset{\displaystyle R^{22}}{\underset{\displaystyle R^{23}_m}{L^3}}- \qquad -\overset{\displaystyle R^{24}}{\underset{\displaystyle R^{25}_m}{L^4}}-\overset{\displaystyle R^{26}}{\underset{\displaystyle R^{27}_m}{L^5}}-\overset{\displaystyle R^{28}}{\underset{\displaystyle R^{29}_m}{L^6}}- ,$$

where

L^1-L^6 are silicon or carbon, not more than two of L^4-L^6 are silicon and m=0 if any two of the vicinal radicals R^{20}, R^{22}, R^{24}, R^{26} and R^{28} form an aromatic ring or a double bond is formed between two adjacent L^2-L^6, and otherwise m=1,

X   are, independently of one another, fluorine, chlorine, bromine, iodine, hydrogen, C_1-C_{10}-alkyl, C_2-C_{10}-alkenyl, C_6-C_{20}-aryl, alkylaryl having 1-10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part, $NR^{30}R^{31}$, OR^{30}, SR^{30}, SO_3R^{30}, $OC(O)R^{30}$, CN, SCN, =O, β-diketonate, BF_4-, PF_6- or bulky noncoordinating anions,

$R^{16}-R^{31}$ are hydrogen, C_1-C_{20}-alkyl, 5- to 7-membered cycloalkyl which may in turn bear a C_6-C_{10}-aryl group as substituent, C_2-C_{20}-alkenyl, C_6-C_{20}-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part, SiR^{32}_3, where the organic radicals $R^{16}-R^{31}$ may be substituted by halogen(s) and any two geminal or vicinal radicals $R^{16}-R^{31}$ may also be joined to form a five- or six-membered ring,

R^{32} are, independently of one another, hydrogen, C_1-C_{20}-alkyl, 5- to 7-membered cycloalkyl which may in turn bear a C_6-C_{10}-aryl group as substituent, C_2-C_{20}-alkenyl, C_6-C_{20}-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and 6-20 carbon atoms in the aryl part and any two geminal radicals R^{32} may also be joined to form a five- or six-membered ring,

n   is a number from 1 to 4 which corresponds to the oxidation state of M or, if D is covalently bound to the metal center M, the oxidation state of M minus the number

of groups D covalently bound to M, and, furthermore, the
value of n is reduced by 1 for each X=oxygen.

Preference is here given to compounds in which A^1, A^2 and A^3 are
5 each a nitrogen atom.

The bridges B^1–B^3 connecting A^1–A^3 can influence the activity and
molecular weight by means of a change in the ring size. Here,
B^1–B^3 are formed by a carbon- and/or silicon-containing divalent
10 organic radical having a chain length of from 1 to 3. B^1–B^3 are
preferably identical. Compounds in which B^1–B^3 are either a
divalent CR^4R^5 or CR^6R^7–CR^8R^9 radical can be prepared very simply
and are therefore preferred. Very particular preference is given
to R^4–R^9 being hydrogen atoms.

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Varying the substituents R^1–R^{15} on the tridentate macrocycle also
allows various properties of the catalyst system to be altered.
The number and type of the substituents can influence the
accessibility of the metal atom M to the olefins to be
20 polymerized. This makes it possible to modify the activity and
selectivity of the catalyst in respect of various monomers, in
particular bulky monomers. Since the substituents can also
influence the rate of termination reactions of the growing
polymer chain, this also enables the molecular weight of the
25 polymers formed to be altered. The chemical structure of the
substituents R^1 to R^{15} can therefore be varied within a wide range
in order to achieve the desired results and to obtain a tailored
catalyst system. Examples of suitable carboorganic substituents
are: C_1–C_{20}-alkyl, which may be linear or branched, e.g. methyl,
30 ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl,
n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl or
n-dodecyl, 5- to 7-membered cycloalkyl which may in turn bear a
C_6–C_{10}-aryl group as substituent, e.g. cyclopropane, cyclobutane,
cyclopentane, cyclohexane, cycloheptane, cyclooctane, cyclononane
35 or cyclododecane, C_2–C_{20}-alkenyl, which may be linear, cyclic or
branched and have an internal or terminal double bond, e.g.
vinyl, 1-allyl, 2-allyl, 3-allyl, butenyl, pentenyl, hexenyl,
cyclopentenyl, cyclohexenyl, cyclooctenyl or cyclooctadienyl,
C_6–C_{20}-aryl which may bear further alkyl groups as substituents,
40 e.g. phenyl, naphthyl, biphenyl, anthranyl, o-, m-,
p-methylphenyl, 2,3-, 2,4-, 2,5- or 2,6-dimethylphenyl, 2,3,4-,
2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- or 3,4,5-trimethylphenyl, or
arylalkyl which may bear further alkyl groups as substituents,
e.g. benzyl, o-, m-, p-methylbenzyl, 1- or 2-ethylphenyl, where
45 two R^1 to R^{15} may also be joined to form a 5- or 6-membered ring
and the organic radicals R^1–R^{15} may also be substituted by
halogens such as fluorine, chlorine or bromine. In the case of

organosilicon substituents SiR^{32}_3, suitable radicals R^{32} are the same radicals as have been set forth in more detail above for R^1-R^{15}, where two R^{32} may also be joined to form a 5- or 6-membered ring, for example trimethylsilyl, triethylsilyl,
5 butyldimethylsilyl, tributylsilyl, triallylsilyl, triphenylsilyl or dimethylphenylsilyl.

According to the present invention, at least one of these radicals R^1-R^{15} has to be a radical $-Z-D$. The donor function D is
10 covalently bound to the metal center M when D is anionic (e.g. an amide, alkoxide or thiolate). If the donor function is uncharged, it can be bound coordinatively to the metal center M or may not coordinate. If a plurality of donor functions D are present, one or more of these can be bound intramolecularly to the metal
15 center M. Preferably, at least one D is bound intramolecularly to the metal center M. If a plurality of donor functions D are present and these are covalently bound intramolecularly to the transition metal M, their maximum number is given by the oxidation state of the metal center minus 1 (since n is at least
20 1). The number of radicals $-Z-D$ is preferably one or two and very particularly preferably one.

Particularly for preparing polyethylene or for preparing copolymers of ethylene with higher α-olefins, it is advantageous
25 to use macrocyclic ligands having simple substitution patterns. In a preferred embodiment, in which the ligand is also simple to prepare, from one to three radicals R^1-R^3 can be $-Z-D$. Particularly preferably, only R^1 is a radical $-Z-D$. The remaining radicals R^2-R^3 are in this case preferably hydrogen, methyl,
30 ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, allyl, benzyl, phenyl, ortho-dialkyl- or ortho-dichloro-substituted phenyls, trialkyl- or trichloro-substituted phenyls, naphthyl, biphenyl and anthranyl. Particularly suitable organosilicon substituents are
35 trialkylsilyl groups having from 1 to 10 carbon atoms in the alkyl radical, in particular trimethylsilyl groups.

As in the case of the metallocenes, the transition metal complexes may be chiral. Thus, the ligand may have one or more
40 chiral centers or else the ligand itself may be only prochiral so that chirality is induced only by it being bound to the transition metal M. This can be achieved readily by, for example, unsymmetrical substitution of the atoms A. Three different nonchiral substituents R^1-R^3 are sufficient to enable R and S
45 enantiomers of the transition metal complexes to be obtained.

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D together with the radical Z bearing it may form an amide NR^{16},
amine $NR^{16}R^{17}$, ether OR^{16}, alkoxide O, thiolate S, thioether SR^{16},
phosphine $PR^{16}R^{17}$, sulfonyl SO_3R^{16}, carboxylate CO_2, carboxylic
ester $OC(O)R^{16}$, ketone $C(O)R^{16}$, imine $C(NR^{16})R^{17}$, nitrile CN or a
5 five- or six-membered heterocyclic ring system such as pyridine,
pyrimidine, quinoline, imidazole, pyrrole, pyrazole, indole,
furan or thiophene. The naming as an anionic group, e.g. alkoxide
or amide, was chosen because in this case the group binds to the
transition metal. Because they are simple to prepare, preference
10 is given to amide, alkoxide, ether, carboxylate and pyridine.
Particular preference is given to using metal complexes in which
D is oxygen, NR^{16}, $NR^{16}R^{17}$ or CN. Appropriate selection of the
radicals R^{16} and R^{17} can likewise exert an influence on the
activity of the catalyst and on the molecular weight of the
15 polymer formed. Suitable carboorganic substituents R^{16} and R^{17} are
the same radicals as described for R^1–R^{15} (apart from -Z-D), where
two radicals R^{16} and R^{17} may also be joined to form a 5- or
6-membered ring and may also be substituted by halogens such as
fluorine, chlorine or bromine. Preferred radicals R^{16} and R^{17} are
20 methyl, ethyl, n-propyl, n-butyl, tert-butyl, n-pentyl, n-hexyl,
n-heptyl, n-octyl, vinyl, allyl, benzyl, phenyl, ortho-dialkyl-
and ortho-dichloro-substituted phenyls, ortho- and para-trialkyl-
and trichloro-substituted phenyls, naphthyl, biphenyl and
anthranyl. Particularly suitable organosilicon substituents are
25 trialkylsilyl groups having from 1 to 10 carbon atoms in the
alkyl radical, in particular trimethylsilyl groups.

The bridge Z between the macrocycle and the functional group D is
a divalent organic radical comprising carbon and/or silicon units
30 and having a chain length of from 1 to 3. Altering the chain
length can influence the activity of the catalyst. Thus, for
example, the ability of the donor D to bind intramolecularly to
the transition metal M is influenced by the length of Z. Suitable
carboorganic substituents R^{18} to R^{29} are the same radicals as
35 described for R^1–R^{15} (apart from Z-D). Preference is here given to
bridge lengths of from 1 to 3 and very particular preference is
given to dimethylsilanediyl or substituted 1,2-ethanediyls and
1,3-propanediyls.

40 The substituents X are determined by the choice of corresponding
metal starting compounds which are used for the synthesis of the
metal complexes. Particularly useful substituents X are halogens
such as fluorine, chlorine, bromine or iodine, in particular
chlorine. Simple alkyl radicals such as methyl, ethyl, propyl,
45 butyl, vinyl, allyl, phenyl or benzyl are also advantageous
ligands X. Examples, which are by no means exhaustive, of further
ligands X are trifluoroacetate, BF_4^-, PF_6^- and also

noncoordinating anions (see, for example, S. Strauss in Chem. Rev. 1993, 93, 927-942) such as $B(C_6F_5)_4{}^-$. The naming of the ligands X as anions does not imply a particular type of bonding to the transition metal M. If X is, for example, a

5 noncoordinating or weakly coordinating anion, the interaction between the metal M and the ligand X tends to be electrostatic in nature. In contrast, if X is, for example, alkyl, the bond is covalent. The various types of bonding are known to those skilled in the art.

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Amides, alkoxides, sulfonates, carboxylates and β-diketonates are particularly useful. Varying the radicals R^{30} and R^{31} makes it possible to make a fine adjustment in, for example, physical properties such as solubility. R^{30} and R^{31} are the same radicals

15 as described for R^1-R^{15} (apart from Z-D). Preference is given to using C_1-C_{10}-alkyl such as methyl, ethyl, n-propyl, n-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl and also vinyl, allyl, benzyl and phenyl as radicals R^{30} and R^{31}. Some of these substituted ligands X are very particularly preferably used since

20 they are obtainable from cheap and readily available starting materials. Thus, a particularly preferred embodiment is obtained when X is dimethylamide, methoxide, ethoxide, isopropoxide, phenoxide, naphthoxide, triflate, p-toluenesulfonate, acetate, acetylacetonate or 1,1,1,5,5,5-hexafluoroacetylacetonate.

25

The number n of the ligands X depends on the oxidation state of the transition metal M. The number n can thus not be given generally, but can assume different values for each particular transition metal. The oxidation states of the individual

30 transition metals in catalytically active complexes are usually known to those skilled in the art. Thus, the appropriate complexes of titanium, of zirconium and of hafnium have, in particular, the oxidation states +3 and +4, chromium, molybdenum and tungsten are preferably present in the oxidation state +3,

35 while iron and nickel are preferably used in the oxidation state +2. However, it is also possible to use complexes whose oxidation state does not correspond to that of the active catalyst. Such complexes can then be appropriately reduced or oxidized by means of suitable activators.

40

Possible transition metals M are, in particular, the elements of groups 3 to 8 of the Periodic Table and especially the elements of group 6 of the Periodic Table. Particularly useful central atoms in the transition metal complexes used according to the

45 present invention are the elements scandium, yttrium, titanium, zirconium, hafnium, vanadium, chromium, molybdenum, tungsten,

manganese, iron, cobalt, rhodium, nickel and palladium. Very particular preference is given to using complexes of chromium.

The preparation of various functional triazacycloalkane ligands
5 has been known for a long time. Various synthetic routes for these complexing ligands are described, for example, in F. Weitl, K. Raymond JACS 101 (1979), 2728; M. Takahashi, S. Takamoto, Bull. Chem. Soc. Japan 50, (1977), 3413; T. Arishima, K. Hamada, S. Takamoto, Nippon Kagaku Kaishi, (1973), 1119; L. Christiansen,
10 D. N. Hendrickson, H. Toftlund, S. R. Wilson, C. L. Xie, Inorg. Chem. 25, (1986), 2813; L. R. Gahan, G. A. Lawrence, A. M. Sargeson, Aust. J. Chem. 35, (1982), 1119; B. A. Sayer, J. P. Michael, R. D. Hancock, Inorg. Chim. Acta, 77, (1983), L63; K Wieghardt, U. Bossek, M. Guttmann, J. Weiss, Z. Naturforsch., 38b
15 (1983), 81 and I.A. Fallis et al., Chem. Commun. 1998, 665-667.

The metal complexes, in particular the chromium complexes, can be obtained in a simple way by reacting the corresponding metal salts such as metal chlorides or metal carbonyls with the ligand
20 (e.g. as described in P. Chaudhuri, K. Wieghardt, Prog. Inorg. Chem. 35, (1987), 329 or G. P. Stahley et al., Acta Crystall. C51, (1995), 18-20).

The process of the present invention for the polymerization of
25 olefins can be combined with all industrially known polymerization methods at temperatures in the range from 20 to 300°C and under pressures of from 1 to 4000 bar. The advantageous pressure and temperature ranges for carrying out the process accordingly depend strongly on the polymerization method. Thus,
30 the catalyst systems used according to the present invention can be employed in all known polymerization processes, i.e., for example, in high-pressure polymerization processes in tube reactors or in autoclaves, in suspension polymerization processes, in solution polymerization processes or in gas-phase
35 polymerization. In the case of high-pressure polymerization processes, which are customarily carried out at pressures of from 1000 to 4000 bar, in particular from 2000 to 3500 bar, high polymerization temperatures are generally also set. Advantageous temperature ranges for these high-pressure polymerization
40 processes are from 200 to 280°C, in particular from 220 to 270°C. In low-pressure polymerization processes, it is usual to employ a temperature which is at least a few degrees below the softening temperature of the polymer. In particular, these polymerization processes are carried out at from 50 to 180°C, preferably from 70
45 to 120°C. Among the polymerization methods mentioned, particular preference is given according to the present invention to gas-phase polymerization, in particular in gas-phase

fluidized-bed reactors, and to suspension polymerization, in
particular in loop reactors and stirred tank reactors. The
gas-phase polymerization can also be carried out in the
condensed, supercondensed or supercritical mode. If desired,
5 different or like polymerization processes can also be connected
in series so as to form a polymerization cascade. Furthermore, an
additive such as hydrogen can also be used in the polymerization
processes to regulate the polymer properties.

10 The process of the present invention allows various olefinically
unsaturated compounds to be polymerized. Here, polymerization
includes copolymerization. In contrast to some known iron and
cobalt complexes, the transition metal complexes used according
to the present invention display good polymerization activities
15 even toward higher α-olefins, so that their suitability for
copolymerization deserves particular emphasis. Suitable olefins
are ethylene and α-olefins having from 3 to 10 carbon atoms, for
example propene, 1-butene, 1-pentene, 1-hexene, 1-heptene,
1-octene or 1-decene, and also internal olefins such as
20 2-pentene, 2-hexene, 3-hexene or norbornene and nonconjugated and
conjugated dienes such as butadiene, 1,5-hexadiene or
1,6-heptadiene and polar monomers such as acrylic esters,
acrolein, acrylonitrile, vinyl ethers, allyl ethers and vinyl
acetate. Vinylaromatic compounds such as styrene can also be
25 polymerized by the process of the present invention. Preference
is given to polymerizing at least one olefin selected from the
group consisting of ethene, propene, 1-butene, 1-pentene,
1-hexene, 1-heptene and 1-octene. In a preferred embodiment of
the process of the present invention, mixtures of ethylene with
30 C_3-C_8-α-olefins are used as monomers.

Some of the metal complexes mentioned as component (A) are
themselves not polymerization-active or only slightly
polymerization-active and are then brought into contact with an
35 activator, namely the component (B), in order to be able to
display good polymerization activity. Examples of suitable
activator compounds are those of the aluminoxane type, in
particular methylaluminoxane. Aluminoxanes are prepared, for
example, by controlled addition of water to alkylaluminum
40 compounds, in particular trimethylaluminum. Aluminoxane
preparations suitable as cocatalyst are commercially available.
It is assumed that these are a mixture of cyclic and linear
compounds. The cyclic aluminoxanes can be represented by the
formula $(R^{33}AlO)_k$ and the linear aluminoxanes can be represented
45 by the formula $R^{33}(R^{33}AlO)_k$, where k indicates the degree of
oligomerization and is a number from about 2 to 50. Advantageous
aluminoxanes consist essentially of aluminoxane oligomers having

a degree of oligomerization of from about 2 to 30 and R^{33} is preferably a C_1-C_6-alkyl group, particularly preferably methyl, ethyl, butyl or isobutyl.

5 Apart from the aluminoxanes, further useful activator components are those which are used in the cationic activation of metallocene complexes. Such activator components are known, for example, from EP-B1-0468537 and from EP-B1-0427697. In particular, it is possible to use boranes or borates such as
10 trialkylborane, triarylborane, dimethylanilinium tetraarylborate, trityl tetraarylborate, dimethylanilinium boratabenzenes or trityl boratabenzenes (see WO-A-97/36937) as activator compounds (B) of this type. Particular preference is given to using boranes or borates which bear at least two perfluorinated aryl radicals.
15 Particularly suitable activator compounds (B) are compounds selected from the group consisting of aluminoxane, dimethylanilinium tetrakispentafluorophenylborate, trityl tetrakispentafluorophenylborate and trispentafluorophenylborane.

20 Further activator components which can be used are compounds such as aluminum alkyls, in particular trimethylaluminum, triethylaluminum, triisobutylaluminum, tributylaluminum, dimethylaluminum chloride, dimethylaluminum fluoride, methylaluminum dichloride, methylaluminum sesquichloride or
25 diethylaluminum chloride, or aluminum trifluoride.

It is sometimes desirable to use a combination of various activators. This is known, for example, in the case of metallocenes where boranes and borates are often used in
30 combination with an aluminum alkyl. A combination of various activator components with the transition metal complex of the present invention is generally also possible.

The amount of activator compound used depends on the type of
35 activator. The molar ratio of metal complex (A) to activator compound (B) can generally be from 1:0.1 to 1:10,000; preference is given to a ratio of from 1:1 to 1:1000. The molar ratio of metal complex (A) to dimethylanilinium tetrakispentafluorophenylborate, trityl
40 tetrakispentafluorophenylborate or trispentafluorophenylborane is preferably from 1:1 to 1:20 and particularly preferably from 1:1 to 1:5, and to methylaluminoxane preferably from 1:1 to 1:3000 and particularly preferably from 1:10 to 1:500. It is also possible for the activator to react with the functional
45 substituent or D to form a bond.

The transition metal complex can be brought into contact with the
activator compound or compounds either before or after being
brought into contact with the olefins to be polymerized.
Preactivation using one or more activator compounds prior to
5 mixing with the olefin and further addition of the same or other
activator compounds after bringing this mixture into contact with
the olefin is also possible. A preactivation is generally carried
out at 10-100°C, preferably 20-80°C.

10 It is also possible for more than one of the transition metal
complexes (A) of the present invention to be simultaneously
brought into contact with the olefin to be polymerized. This has
the advantage that a wider range of polymers can be produced in
this way. For example, bimodal products can be produced.

15
A likewise broad range of products can be obtained by use of the
complexes (A) in the presence of a catalyst (C) customary for the
polymerization of olefins. Catalysts (C) which can be used for
this purpose are, in particular, classical Ziegler-Natta
20 catalysts based on titanium, classical Phillips catalysts based
on chromium oxides, metallocenes, constrained geometry complexes
(see, for example, EP-A-416815 or EP-A-420436), nickel and
palladium bisimine systems (for the preparation of these, see
WO-A-98/03559), iron and cobalt pyridinebisimine compounds (for
25 the preparation of these, see WO-A-98/27124) or chromium-pyrrole
compounds (see, for example, EP-A-608447). This makes it
possible, for example, to prepare bimodal products or generate
comonomers in situ by means of such combinations.

30 The catalysts (A) of the present invention can also, if desired,
be immobilized on an organic or inorganic support and be used in
supported form in the polymerization. This is a customary method
of avoiding deposits in the reactor and of controlling the
polymer morphology. As support materials, preference is given to
35 using silica gel, magnesium chloride, aluminum oxide, mesoporous
materials, aluminosilicates and organic polymers such as
polyethylene, polypropylene or polystyrene, in particular silica
gel or magnesium chloride.

40 The activator compounds (B) and the polymerization catalyst (A)
can be brought into contact with the support in various orders or
simultaneously. This is generally carried out in an inert solvent
which, after the immobilization, can be removed by filtration or
evaporation. The use of supported catalysts which are still moist
45 is also possible. Thus, the mixture of the support with the
activator compound or compounds can be carried out first or the
support can first be brought into contact with the polymerization

catalyst. Preactivation of the catalyst using one or more
activator compounds prior to mixing with the support is also
possible. The amount of metal complex (A) (in mmol) per gram of
support material can vary greatly, e.g. in the range from 0.001
5 to 1 mmol/g. The preferred amount of metal complex (A) per gram
of support material is from 0.001 to 0.5 mmol/g, particularly
preferably from 0.005 to 0.1 mmol/g. In one possible embodiment,
the metal complex (A) can also be prepared in the presence of the
support material. A further method of immobilization is
10 prepolymerization of the catalyst system with or without prior
application to a support.

The process of the present invention allows polymers of olefins
to be prepared. For the purposes of the present invention, the
15 term polymerization encompasses both polymerization and
oligomerization, i.e. oligomers and polymers having molecular
weights in the range from about 56 to 3,000,000 can be produced
by this process.

20 Owing to their good mechanical properties, the polymers prepared
using the catalyst system of the present invention are especially
suitable for producing films, fibers and moldings.

The catalysts of the present invention have good activities.
25 Comparison of the polymerization results of
N,N',N''-trimethyl-1,4,7-triazacyclononanechromium trichloride
with those of an analogous compound bearing the additional
donor-functionalized substituents gives the following surprising
result: while the first-named catalyst gives only dimers,
30 polymers having molecular weights around 200,000 are obtained
when using the latter catalyst.

The following examples illustrate the invention.

35 All work was, unless otherwise indicated, carried out with
exclusion of air and moisture. Toluene and tetrahydrofuran (THF)
were dried by means of a molecular sieve column or
sodium/benzophenone and distilled. Triisobutylaluminum TiBAl (2 M
in heptane) was obtained from Witco, MAO (methylaluminoxane, 10%
40 in toluene) and N,N-dimethylanilinium
tetrakis(pentafluorophenyl)borate (DMAB) were obtained from
Albemarle, MAO (methylaluminoxane, 30% in toluene) was obtained
from Witco GmbH, n-butyllithium (2.5M in hexane) was obtained
from Aldrich and n-butyllithium (2.5M in hexane) was obtained
45 from Acros.

14

The preparation of N-(1,4,7-triazacyclononanyl)-2-octan-2-ol was carried out as described by I.A. Fallis et al., Chem. Commun. 1998, 665-667.

5 Example 1:

Preparation of
(1-(2-oxidooctyl)-1,4,7-triazacyclononanyl)chromium(III) dichloride

10
2 ml (3 mmol) of a solution of 1.5M butyllithium in hexane were slowly added dropwise at -30°C to a solution of 804 mg (3.12 mmol) of 1-(2-hydroxyoctyl)-1,4,7-triazacyclononane in THF over a period of 30 minutes. After addition was complete, the mixture
15 was warmed to room temperature and 1105 mg (2.95 mmol) of CrCl₃(THF)₃ were then added. The reaction mixture was filtered through a short silica gel column and subsequently freed of all volatile constituents in an oilpump vacuum. This gave a pulverulent product in a yield of 75% (907 mg; 2.21 mmol).

20
Example 2:

2.1. Preparation of
1,3-didodecyl-5-(3-dimethylaminopropyl)-1,3,5-triazacyclohexane

25
10.7 g of dodecylamine (58 mmol) and 0.8 ml of 3-dimethylaminopropylamine (6.4 mmol) were dissolved in ethanol, after which 1.93 g of paraformaldehyde (64 mmol) were added and the mixture was stirred. The turbidity which developed was
30 redissolved every now and again by addition of ether. After about 1 day, all the paraformaldehyde had dissolved. The solvent was subsequently removed on a rotary evaporator, the residue was dissolved in a little toluene and the product was then again freed of solvent under reduced pressure. This left 12.27 g of a
35 viscous, colorless product which, according to NMR spectroscopy, consisted of about 75 mol% of 1,3,5-tridodecyl-1,3,5-triazacyclohexane and 25 mol% of 1,3-didodecyl-5-(3-dimethylaminopropyl)-1,3,5-triazacyclohexane and toluene.

40
Ligand mixture:

13C-NMR (50 MHz, CDCl₃): δ 74.5 (ring CH₂), 57.6, 50.5 (NCH₂ (amine)), 52.6 (NCH₂ (dodecyl)), 45.3 (NMe₂), 31.7, 29.3-29.6,
45 27.4, 27.3, 22.6 (CH₂), 19.9 (Me (methyl))

2.2. Preparation of
1,3-didodecyl-5-(3-dimethylaminopropyl)-1,3,5-triazacyclohexane-
chromium trichloride

5 11.85 g of the above mixture (96.6%) were dissolved in 300 ml of
toluene, and 3.24 g of CrCl$_3$ (20.5 mmol) were subsequently added.
After distilling off 50 ml of toluene, 0.3 g of Zn powder was
added. The solvent was then removed by distillation and the
residue was washed with ether. Further purification was carried
10 out by column chromatography over silica gel. Elution was first
carried out using chloroform and 11 g of
1,3,5-tridodecyl-1,3,5-triazacyclohexanechromium trichloride
(14.7 mmol, 95% of theory) were obtained, after which the eluent
was changed to acetone and 1.2 g of
15 1,3-didodecyl-5-(3-dimethylaminopropyl)-1,3,5-triazacyclohexane-
chromium trichloride (1.8 mmol, 30%) were obtained.

Example 3:

20 3.1. Preparation of
1,3-diethyl-5-(2-cyanoethyl)-1,3,5-triazacyclohexane

Method I:

25 1 ml of 3-aminopropionitrile (14 mmol) was dissolved in 80 ml of
1,3,5-triethyl-1,3,5-triazacyclohexane (0.4 mol) and the solution
was heated at 130°C for 12 hours. After distilling off the excess
1,3,5-triethyl-1,3,5-triazacyclohexane at 70°C/1.3 Pa, 2.2 g of
crude product were obtained. This was dissolved in 50 ml of ether
30 and filtered through a short silica gel column. Removing the
solvent under reduced pressure left 1.9 g (69%) of a colorless
oil.

Method II:

35
9 ml of 3-aminopropionitrile (130 mmol) and 100 ml of ethylamine
(70% strength in water, 1.2 mol) were dissolved in 200 ml of
ethanol, then 40 g of paraformaldehyde (1.33 mol) were added and
the mixture was stirred. After dissolution of the
40 paraformaldehyde and cooling to room temperature, the solvent was
removed, the residue was dissolved in 50 ml of ether and filtered
through a short silica gel column. Removal of the solvent under
reduced pressure left 20 g (78%) of a colorless oil.

45 MS (70 eV, 23°C): 196 (M$^+$, 8%), 195 ((M-H)$^+$, 11%), 139
((M-(H$_2$C=NEt (Et: ethyl)))$^+$, 27%)

16

1H-NMR (200 MHz, CDCl$_3$): δ 3.3, 3.2br (6H, ring CH$_2$), 2.9t (2H, CH$_2$CH$_2$CN), 2.4t (2H, CH$_2$CH$_2$CN), 2.2q (4H, CH$_2$Me), 0.9t (6H, CH$_2$Me)

13C-NMR (50 MHz, CDCl$_3$): δ 118.7 (CN), 74.5, 73.1 (ring CH$_2$), 48.3 (CH$_2$CH$_2$CN), 46.1 (CH$_2$Me), 17.5 (CH$_2$CH$_2$CN), 12.1 (CH$_2$Me)

IR (KBr, v/cm^{-1}): 649m, 805m, 1008s, 1045s, 1104m, 1122m, 1146w, 1189m, 1215m, 1292s, 1356m, 1379m, 1454s, 1470s, 2247m, 2642m, 2790s, 2806s, 2874s, 2936s, 2969s

3.2. Preparation of
1,3-diethyl-5-(2-cyanoethyl)-1,3,5-triazacyclohexanechromium
trichloride

2.2 g (11.2 mmol) of
1,3-diethyl-5-(2-cyanoethyl)-1,3,5-triazacyclohexane and 4.0 g of
CrCl$_3$(THF)$_3$ (11 mmol) were stirred in 40 ml of THF. After 1 hour,
the solvent was removed under reduced pressure, fresh THF was
added twice and removed under reduced pressure, and the residue
was then washed with ether and dried under reduced pressure. This
gave 1.9 g of violet
1,3-diethyl-5-(2-cyanoethyl)-1,3,5-triazacyclohexanechromium
trichloride (88%), melting point: 246-248°C.

Elemental analysis (calc.): C 34.0 (33.9), H 6.0 (5.7), N 15.0
(15.8), Cl 26.4 (30.0)

IR (KBr, v/cm^{-1}): 423m, 431m, 504m, 508m, 516m, 531w, 547m, 602m,
763m, 793m, 924w, 964m, 983s, 1006s, 1020s, 1086m, 1097m, 1121w,
1141s, 1170s, 1202m, 1245s, 1270s, 1292s, 1303s, 1323s, 1331s,
1348s, 1377s, 1391s, 1414m, 1462m, 1486s, 1639s, 2254m, 2887s,
2953s, 2983s, 3390s

Example 4:

4.1. Preparation of
1,3-didodecyl-5-(2-hydroxyethyl)-1,3,5-triazacyclohexane

48 g of dodecylamine (259 mmol) and 1.7 ml of ethanolamine
(29 mmol) were dissolved in 100 ml of ethanol, after which 8.6 g
of paraformaldehyde (287 mmol) were added and the mixture was
stirred. The turbidity caused by
1,3,5-tridodecyl-1,3,5-triazacyclohexane was redissolved every
now and again by addition of ether. After about 1 day, all the
paraformaldehyde had dissolved. The solvent was then removed on a
rotary evaporator, the residue was dissolved in a little toluene
and the product was then again freed of solvent under reduced

17

pressure. This left 55 g of a viscous colorless product which, according to NMR spectroscopy, consisted of about 75 mol% of 1,3,5-tridodecyl-1,3,5-triazacyclohexane and 25 mol% of 1,3-didodecyl-5-(2-hydroxyethyl)-1,3,5-triazacyclohexane and a
5 little toluene.

4.2. Preparation of
1,3-didodecyl-5-(2-oxidoethyl)-1,3,5-triazacyclohexanechromium dichloride
10
2.6 g of the above mixture were reacted with 0.7 g of $CrCl_3$ (4.4 mmol) in toluene and 0.3 g of Zn powder as described under 2.2. After 2 hours, 50 ml of THF were added, the mixture was again heated to boiling and then stirred for 2 days. After
15 removing the solvent and washing with ether, the green-violet residue was purified by column chromatography over silica gel. Elution was first carried out using dichloromethane and 590 mg of 1,3,5-tridodecyl-1,3,5-triazacyclohexanechromium trichloride (0.8 mmol) were obtained, after which the eluent was changed to
20 acetone and 1.8 g of green 1,3-didodecyl-5-(2-oxidoethyl)-1,3,5-triazacyclohexanechromium dichloride product (3.1 mmol, 70%) were obtained. To purify the green product, it was dissolved in hexane and reprecipitated by cooling to −20°C.
25
Example 5:

5.1. Preparation of
1,3-didodecyl-5-(2-dimethylaminoethyl)-1,3,5-triazacyclohexane
30 (5.1.a) and
1-dodecyl-3,5-bis(2-dimethylaminoethyl)-1,3,5-triazacyclohexane
(5.1.b)

20.16 g of dodecylamine (109 mmol) and 5.9 ml of
35 dimethylaminoethylamine (54 mmol) were dissolved in ethanol, then 4.90 g of paraformaldehyde (163 mmol) were added and the mixture was stirred. After about 1 day, all the paraformaldehyde had dissolved. The solvent was then removed on a rotary evaporator, the residue was dissolved in a little toluene and was then again
40 freed of solvent under reduced pressure.

5.2. Preparation of
1,3-didodecyl-5-(2-dimethylaminoethyl)-1,3,5-triazacyclohexane-chromium trichloride (5.2.a) and
45 1-dodecyl-3,5-bis(2-dimethylaminoethyl)-1,3,5-triazacyclohexane-chromium trichloride (5.2.b)

The above mixture was reacted with 8.2 g of $CrCl_3$ (52 mmol) and 0.45 g of Zn powder as described under 2.2. After removing the solvent and washing with ether, the residue was extracted a number of times with acetone (solution A) and then with

5 chloroform (solution B).

The solvent was removed from solution A under reduced pressure and the residue was chromatographed on silica gel. Elution was first carried out using chloroform and 3.9 g of (A1) were

10 obtained, then using acetone to give 3.62 g of (A2) and using acetone/triethylamine to give a further 2.40 g of (A3). (A1) was chromatographed together with solution B on silica gel. Elution was first carried out using chloroform and 12.12 g of 1,3,5-tridodecyl-1,3,5-triazacyclohexanechromium trichloride

15 (16 mmol) were obtained, then using acetone to give 3.96 g of (B2). (A2) was again purified by chromatography using acetone and 2.11 g of (C2) were obtained. (A3) was, after removing the solvent, separated chromatographically using acetone into 400 mg of (D2) and then 1.28 g of (D3). The fractions (B2), (C2) and

20 (D2) were combined and again purified by chromatography using acetone, then dissolved in a little toluene, freed of solvent under reduced pressure, washed with pentane and again dried under reduced pressure. This gave 4.84 g of 1,3-didodecyl-5-(2-dimethylaminoethyl)-1,3,5-triazacyclohexane-

25 chromium trichloride (5.2.a) (7.4 mmol). The fraction (D3) was purified by chromatographing it again using acetone and 1.06 g of 1-dodecyl-3,5-bis(2-dimethylaminoethyl)-1,3,5-triazacyclohexane-chromium trichloride (5.2.b) (1.9 mmol) were obtained.

30 Example 6:

Preparation of
1,3,5-tris(3-(3-ethylhexyloxy)propyl)-1,3,5-triazacyclohexane

35 The preparation was carried out by a method analagous to that described in C. W. Hoerr et. al. J. Am. Chem. Soc. 78, (1956), 4667-4670, using 3-(3-ethylhexyloxy)propylamine in place of dodecylamine.

40 1H-NMR (200 MHz, $CDCl_3$): δ 3.3t (6H, OCH_2), 3.1d (6H, OCH_2), 3.2br (6H, ring (H_2), 2.3t (6H, NCH_2), 1.0-1.6 (33H, CH, CH_2), 0.7t (12H, Me)

13C-NMR (50 MHz, toluene): δ 73.7 (ring CH_2), 72.4, 67.9 (OCH_2),
45 48.4 (NCH_2), 39.0 (CH), 30.0, 28.4, 27.4, 23.2, 22.3 (CH_2), 13.2, 10.3 (Me)

Example 7:

Preparation of
1,3,5-tris(3-(2-methoxyethoxy)propyl)-1,3,5-triazacyclohexane

The preparation was carried out by a method analogous to that
described by C. W. Hoerr et. al., J. Am. Chem. Soc. 78, (1956),
4667-4670, using 3-propylamino-2-methoxyethyl ether in place of
dodecylamine.

1H-NMR (200 MHz, CDCl$_3$): δ 3.35-3.50 (18H, OCH$_2$), 3.30 (9H, OCH$_3$),
3.2br (6H, ring CH$_2$), 2.4t (6H, NCH$_2$), 1.6t (6H, C-CH$_2$-C)

13C-NMR (50 MHz, CDCl$_3$): δ 74.3 (ring CH$_2$), 71.6, 69.8, 69.3
(OCH$_2$), 58.7 (OCH$_3$), 49.2 (NCH$_2$), 27.4 (C-CH$_2$-C)

Example 8:

8.1 Preparation of
1,3-dimethyl-5-(2-hydroxyethyl)-1,3,5-triazacyclohexane

1 ml of ethanolamine (17 mmol) was dissolved in 80 ml of
1,3,5-trimethyl-1,3,5-triazacyclohexane and heated at 130°C for
12 hours (gas evolution). After distilling off the excess
1,3,5-trimethyl-1,3,5-triazacyclohexane (60°C/0.01 torr), 2 g of
crude product were obtained. 10 ml of methylamine (40% in water)
were added, the mixture was stirred for 12 hours and volatiles
were then again removed under reduced pressure. The residue was
vaporized and recondensed under reduced pressure by brief heating
with a Bunsen burner.
Yield: 1.2 g (46%) of a colorless oil.

1H NMR (CDCl$_3$, 200 MHz): 5.35br (1H, HO), 3.50t (2H, HOCH$_2$),
3.14br (6H, NCH$_2$N), 2.79t (2H, NCH$_2$), 1.97s (6H, NMe$_2$)

Using a method analogous to Example 8.1., 1 ml of ethanolamine
(17 mmol) and 80 ml of 1,3,5-triethyl-1,3,5-triazacyclohexane
were used to prepare 1.4 g of
1,3-diethyl-5-(2-hydroxyethyl)-1,3,5-triazacyclohexane:

1H NMR (CDCl$_3$, 200 MHz): 5.74br (1H, HO), 3.62t (2H, CH$_2$OH),
3.29br (6H, NCH$_2$N), 2.85t (2H, NCH$_2$CH$_2$OH), 2.24t (4H, NCH$_2$CH$_3$),
0.99q (4H, NCH$_2$CH$_3$).

8.2. Preparation of
1,3-dimethyl-5-(2-oxidoethyl)-1,3,5-triazacyclohexanechromium
dichloride

5 40 ml of THF were condensed onto 1.0 g of
1,3-dimethyl-5-(2-hydroxyethyl)-1,3,5-triazacyclohexane
(7.7 mmol) and 2.8 g of $CrCl_3(THF)_3$ (7.5 mmol). The suspension was
stirred at room temperature until it became green. After removal
of the solvent under reduced pressure, another 40 ml of THF were
10 condensed onto the residue and the green suspension was stirred
for 1 hour. After again removing the THF, washing twice with
ether and drying under reduced pressure, 1.4 g (91%) of
light-green
1,3-dimethyl-5-(2-oxidoethyl)-1,3,5-triazacyclohexanechromium
15 dichloride product were obtained.

IR (KBr, v/cm^{-1}): 3226m, 2941s, 2899m, 2856m, 2789s, 2729m, 2687m,
2650m, 2604w, 1468w, 1445w, 1429w, 1385m, 1335w, 1258m, 1234s,
1203w, 1147s, 1108s, 1055m, 1034m, 1003s, 983w, 961w, 944w,
20 917s, 899m, 862w, 837w, 795w, 655w, 616w

Examples 9 to 21:

Polymerizations
25
A solution of the complex indicated in Table 1 in 250 ml of
toluene was admixed with the appropriate amount of MAO (10%
strength solution in toluene). In the case of activation using
DMAB N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, the
30 amount of DMAB indicated in Table 1 was added, the mixture was
heated to 70°C, then admixed with TiBAl (see Tab. 1) and the
resulting solution was again brought to 40°C. The polymerization
was started by passing in ethylene at a flow rate of from about
20 to 40 l/h at atmospheric pressure at 40°C. After the time
35 indicated in Table 1 under a constant ethylene flow, the
polymerization was stopped by addition of methanolic HCl solution
(15 ml of concentrated hydrochloric acid in 50 ml of methanol).
250 ml of methanol were subsequently added and the white polymer
formed was filtered off, washed with methanol and dried at 70°C.
40
Polymerization data and the corresponding product properties are
shown in Table 1.

The comonomer content of the polymer (%C_6) and its methyl side
45 chain content per 1000 carbon atoms of the polymer chain
(CH_3/1000) were determined by IR spectroscopy.

The η value was determined at 130°C by means of an automatic Ubbelohde viscometer (Lauda PVS 1) using decalin as solvent (ISO1628 at 130°C, 0.001 g/ml of decalin).

5 The molar mass distributions and the means Mn, Mw and Mw/Mn derived therefrom were determined by means of high-temperature gel permeation chromatography using a method based on DIN 55672 under the following conditions: solvent: 1,2,4-trichlorobenzene, flow: 1 ml/min, temperature: 140°C, calibration using PE
10 standards.

Abbreviations in Table 1:

M_w	weight average molecular weight
15	M_n	number average molecular weight
Q	polydispersity (ratio of M_w to M_n)
m.p.	melting point of the polymer
n	Staudinger index (viscosity)
$CH_3/1000$	number of methyl side chains per 1000 carbon atoms

20

25

30

35

40

45

Table 1: Polymerization data and polymer analyses

Ex.	Comp. a)	Amount b) [mg] (μmol)	MAO [mmol]	Al:Cr	Cr:B c)	Activity kg/mol Cr·h	Yield [g] (min) d)	η [dl/g]	Mw [g/mol]	Q	m.p. [°C]	Total CH₃ [/1000C]
9	1.	6.2 (15)	5	330:1		680	10.2 (60)		205282	3.93	129	
10	1	4.1 (10)	5	500:1		850	8.5 (60)		139792	2.75	131	
11	2.2.	22.1(33.1)	11.6	350:1	-	165	5.5 (60)	2.71			127.9	6.4
12	3.2.	15.8(24.1)	8.44	700:1	-	20	0.51 (60)	1.27			133.9	5.7
13	3.2.	14.1(21.5)	21.5	1000:1	-	91	1.96 (60)	2.75			138.0	4.7
14	4.2.	10.0(17.5)	6.12	220:1	-	5	0.25 (60)	2.22				9.2
15	4.2.	21.8(38.0)	19.0	500:1	2.1:1	9	0.35 (60)	-				<1
16	5.2.a	13.6(23.3)	8.2	500:1	-	17	0.4 (60)	1.61			133	2.6
17	5.2.b	17.0(26.0)	9.1	350:1	-	185	4.8 (60)	0.58			127.6	5.6
18	6.	20 (26.8)	7.28	720:1	-	0	0 (60)	-			-	-
19	7.	23.5(39.5)	30.45	1000:1	-	8	0.47 (90)	2.77			126.1	8
20	8.	5.9(21.2)	7.45	351:1	-	11	0.24 (60)	1.13	46729	3.96	134.8	1.8
21	8.	6.0 (21.6)	-	20:1	1:1.4	78	1.68 (60)	1.61	36659	8.59	132	5.3

a)   Comp.= Compound (transition metal complex corresponding to example number)

b)   Amount of the compound

c)   Activation carried out by addition of DMAB and TiBAl

d)   Polymerization time

The polymerization was carried out at 40°C.